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Synthesis of asymmetric supramolecular compounds using a Ni(0) catalysed homo-coupling approach

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The synthesis and characterisation of a series of dinuclear ruthenium and osmium polypyridyl metal complexes based on the bridging ligands [5-(5′-bipyridin-2′,2″-yl)-3-(pyridin-2-yl)]-1,2,4-triazole (Hpytr-bipy), 2,2′-bis(pyridin-2″yl)-5,5′-bis(pyridin-3″-yl) (bipy-bipy) and 5,5′-bis(pyridin-2″-yl)-3,3′-bis(1,2,4-triazole) (Hpytr-Hpytr) are reported. The dinuclear complexes have been synthesised *via* a Ni(0) catalysed cross-coupling reaction from brominated precursors. With this approach a mixture of three products is obtained, which are separated by chromatographic methods. The compounds obtained are characterised by elemental analysis, ^{1}H NMR, absorption and emission spectroscopy. The synthetic approach developed offers a new route to asymmetric multinuclear supramolecular structures that is complimentary to the complexes as ligands/complexes as metal approaches.

Introduction

The development of supramolecular chemistry based on ruthenium and, increasingly, osmium, polypyridyl metal complexes witnessed over the past four decades has led to the definition of molecular entities useful for the construction of multifunctional systems. Their robust tuneable photophysical, photochemical and electrochemical properties constitute the primary basis of interest in these complexes and have led to widespread development and investigation into their application as artificial antenna systems, charge separation devices for photochemical solar energy conversion, and molecular electronics.[1] The development of such applications is greatly dependent on the availability of a synthetic approach capable of delivering organised structures of metal-based molecular components with specific supramolecular properties.[2] The challenges encountered in the preparation of pure, structurally well-defined metal complexes increases with the size of the structure and although the complexes as metals/complexes as ligands approaches have proven remarkably effective there remains a need for the development of alternative synthetic approaches.[3]

We are at present interested in intramolecular processes in asymmetric dinuclear metal complexes, containing two $M(bipy)_2$ units, where M is Ru(II) or Os(II), incorporating a bridging ligand consisting of two different chelating moieties, one bipy and one triazole based, as shown in Fig. 1.

In this contribution we report the syntheses, separation and characterisation of the target dinuclear complexes using a homocoupling reaction. The decision to utilise a nickel catalysed[4] homogeneous coupling approach for the synthesis of asymmetric dinuclear complexes seems, in the first instance, counter-intuitive. The results obtained show, however, that such an approach can prove to be fruitful provided that the mixture of products obtained can be separated in a facile manner. Coupling was carried out employing the ruthenium and osmium precursors $[M(bipy)_2(bipy\text{-}Br)]^{2+}$ (**1a**/**1b**), $[M(bipy)_2(pytr\text{-}Br)]^{+}$ **2a**/**2b** and their selectively deuteriated analogues **1d** and **2d** containing bromo-substituted ligands. With this method binuclear complexes of the types $[M(bipy)_2(bipy\text{-}bipy)M(bipy)_2]^{4+}$ (**3**, **4**), $[M(bipy)_2(pytr\text{-}pytr)M(bipy)_2]^{2+}$ (**5**, **6**), and $[M(bipy)_2(pytr\text{-}bipy)M(bipy)_2]^{3+}$ (**7**, **8**, **9** the target complexes), where (bipy-bipy) is 2,2′-bis(pyridin-2″yl)-5,5′-bis(pyridin-3″-yl), (Hpytr-Hpytr) is 5,5′-bis(pyridin-2″-yl)-3,3′-bis(1,2,4-triazole) and (Hpytr-bipy) is [5-(5′-bipyridin-2′,2″-yl)-3-(pyridin-2-yl)]-1,2,4-triazole and M is either Ru(II) or Os(II) were isolated (Fig. 2).

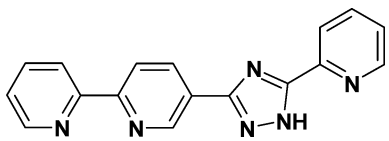

Fig. 1 Structure of target bridging ligand Hpytr-bipy, [5-(5′-bipyridin-2′,2″-yl)-3-(pyridin-2-yl)]-1,2,4-triazole.

The deuteriated ruthenium isotopologues **3d**, **5d** and **7d** are reported also. All compounds are characterised using NMR, UV/Vis and emission spectroscopy.

Experimental

Materials

All solvents used for spectroscopy were of spectroscopic grade (Sigma-Aldrich). All other reagents were of HPLC or Analar grade. *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$[5], *cis*-$[Os(bipy)_2Cl_2]$[6] and *cis*-$[Ru(d_8\text{-}bipy)_2Cl_2]\cdot 2H_2O$[7] and the ligands 5-bromo-1,2,4-triazole (HBrpytr),[3a,b] and 5-bromo-2,2′-bipyridyl (Brbipy)[8] and complexes **2a**, **2b** and **2d**[3a,b] were prepared by methods reported previously.

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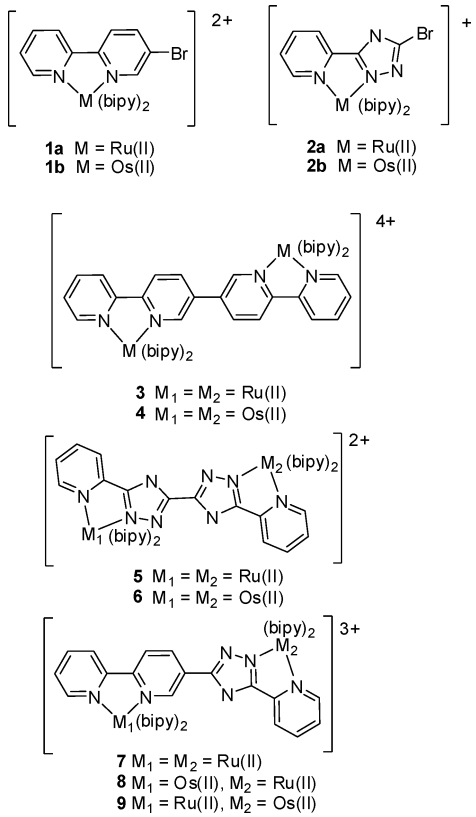

Fig. 2 Structures of the dinuclear complexes and their precursor complexes. The compounds **1d**, **2d**, **3d**, **5d** and **7d** were prepared using $[Ru(d_8\text{-bipy})Cl_2]\cdot 2H_2O$.

Syntheses

$[Ru(bipy)_2(Brbipy)](PF_6)_2$ (**1a**). 185 mg (0.36 mmol) of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ was added to 127 mg (0.54 mmol) Brbipy in 50 cm^3 of a 1 : 1 water–ethanol mixture. The solution was heated at reflux overnight turning the reaction mixture from deep purple to clear red. The solution was reduced *in vacuo* and the product precipitated upon the addition of aqueous NH_4PF_6. The crude product was collected by filtration and washed with diethyl ether. The complex was purified by column chromatography on neutral alumina with acetonitrile as eluent. The product was obtained upon evaporation of the solvent and recrystallised from methanol–water (1 : 1). Yield: 269 mg (0.29 mmol), 76%. ^{1}H NMR (CD_3CN, 298 K) δ 8.50 (5H, m), 8.38 (1H, s), 8.24 (1H, dd), 8.05 (5H, m), 7.80 (2H, d), 7.74 (1H, d), 7.70 (1H, t), 7.65 (1H, dd), 7.40 (6H, m). Elem. anal. $C_{30}H_{23}N_6RuP_2F_{12}$: Calc: C 38.38%, H 2.45%, N 8.95%. Found: C 38.49%, H 2.44%, N 8.71%. ESI-MS $[M - 2PF_6]^{2+}$ $m/z = 324$.

$[Ru(d_8\text{-bipy})_2(Brbipy)](PF_6)_2$ (**1d**) was prepared as reported for **1a** above. Yield: 271 mg, 0.24 mmol, 67.6%. ^{1}H NMR (CD_3CN, 298 K) δ 8.51 (H3′, d), 8.41 (H4′, d), 8.25 (H3, d), 8.08 (dd, H4), 7.77 (H6′, s), 7.73 (H6, d), 7.43, (H5, dd).

$[Os(bipy)_2(Brbipy)](PF_6)_2$ (**1b**). This complex was obtained from *cis*-$[Os(bipy)_2Cl_2]$ as for **2a**. Yield: 135 mg (0.13 mmol), 68%. ^{1}H NMR (CD_3CN, 298 K) δ 8.52–8.5 (m, 5H), 8.4 (d, 1H), 8.05 (dd, 1H), 7.92–7.87 (m, 5H), 7.72 (m, 2H), 7.66–7.57 (m, 4H), 7.36–7.32 (m, 5H). Elem. anal. $C_{30}H_{37}N_6OsP_2F_{12}$: Calc: C 35.05%, H 2.23%, N 8.18%. Found: C 35.05%, H 2.19%, N 7.93%.

Ni(0) coupling reactions using 1a and 2a as precursors

$[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_2$ (**5**), $[Ru(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3$ (**7**) and $[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4$ (**3**). 2.29 g (8.72 mmol) of triphenylphosphine and 10 cm^3 of dry DMF were added to 514.51 mg (2.17 mmol) of nickel(II) chloride. The blue mixture was stirred for 30 min under N_2. 142 mg (2.17 mmol) of zinc powder was added and the mixture was stirred for 1 h, at which stage the solution was brown. 842 mg (1.09 mmol) of $[Ru(bipy)_2(Brpytr)](PF_6)$ (**1a**) and 1.02 g (1.09 mmol) of $[Ru(bipy)_2(Brbipy)](PF_6)_2$ (**2a**) were added to this solution. The mixture was heated at 95 °C for 6 h after which the mixture was diluted with 30 cm^3 of acetonitrile, filtered and flash precipitated from diethyl ether with rapid stirring. The crude product was isolated by filtration Crude yield: 1.12 g. The crude product was then purified by column chromatography on silica gel with acetonitrile–saturated aqueous $NaNO_3$ solution (7 : 5 v/v) to yield three fractions which were identified by ESI-MS. The third fraction contained a mixture of the desired products.

This fraction was further purified by column chromatography on Sephadex-Sp C-25 with NaCl solution (0.05–0.1 M for first band, 0.17–0.25 M for second band, 0.4–0.45 M for third band). Three fractions were obtained with the first fraction being identified as $[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_2$ (**5**) the second fraction as $[Ru(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3$ (**7**) and the final fraction as $[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4$ (**3**). On occasion the third band required further purification on a silica column with acetonitrile–water (4 : 1, v/v) with 0.05 M KNO_3 buffer as eluent. The solutions obtained were reduced *in vacuo* and the product precipitated by the addition of aqueous NH_4PF_6. The products were collected by filtration and washed with diethyl ether and recrystallised from methanol–water (1 : 1).

Fraction 1. $[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_2\cdot 5H_2O$ (**5**). Isolated yield: 8.1%. ^{1}H NMR (CD_3CN, 298 K) δ 8.42 (8H, m), 8.06 (dd, 2H), 7.83–8.02 (m, 14H), 7.78 (m, 4H), 7.49 (d, 2H), 7.27–7.40 (m, 8H), 7.10 (dd, 2H). Elem. anal. $Ru_2C_{54}H_{40}N_{16}P_2F_{12}\cdot 5H_2O$: Calc: C 43.37%, H 3.34%, N 14.99%. Found: C 42.84%, H 3.38%, N 14.94%. ESI-MS $[M - 2PF_6]^{2+}$ $m/z = 556.7$, $[M - 2PF_6 + H^+]^{3+}$ $m/z = 372$.

Fraction 2. $[Ru(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3\cdot 2NaNO_3$ (**7**). Isolated yield: 7.6%. ^{1}H NMR (CD_3CN, 298 K) δ 8.72–8.48 (m, 12H), 8.29 (d, 1H), 8.11–7.95 (m, 10H), 7.84–7.67 (m, 9H), 7.55 (dd, 1H), 7.48–7.37 (m, 9H), 7.24 (dd, 1H). Elem. anal. $Ru_2C_{57}H_{43}N_{14}P_3F_{18}\cdot 2NaNO_3$: Calc: C 39.53%, H 2.48%, N 12.94%. Found: C 38.38%, H 2.44%, N 12.46%.

Fraction 3. $[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4\cdot 2KNO_3$ (**3**). Isolated yield: 8.0%. ^{1}H NMR (CD_3CN, 298 K) δ 8.46–8.59 (m, 12H), 7.78 (d, 2H), 7.70 (d, 4H), 7.43–7.35 (m, 10H). Elem. anal. $Ru_2C_{60}H_{46}N_{12}P_4F_{24}\cdot 2KNO_3$: Calc: C 37.54%, H 2.40%, N 10.22%. Found: C 37.43%, H 2.97%, N 9.60%.

Ni(0) coupling reactions using 1d and 2d as precursors

$[Ru(d_8\text{-bipy})_2(pytr\text{-}pytr)Ru(d_8\text{-bipy})_2](PF_6)_2$ (**5d**), $[Ru(d_8\text{-bipy})_2(pytr\text{-}bipy)Ru(d_8\text{-bipy})_2](PF_6)_3$ (**7d**) and $[Ru(d_8\text{-bipy})_2(bipy\text{-}bipy)Ru(d_8\text{-bipy})_2](PF_6)_4$ (**3d**) were obtained from $[Ru(d_8\text{-bipy})_2(Brpytr)](PF_6)$ (0.16 mmol) and $[Ru(d_8\text{-bipy})_2(Brbipy)](PF_6)_2$

(0.16 mmol) using the method described above. Crude yield: 0.174 g (95%).

Fraction 1. $[Ru(d_8\text{-bipy})_2(pytr\text{-}pytr)Ru(d_8\text{-bipy})_2](PF_6)_2$ (**5d**). Yield after purification: 6.0%. ^1H NMR (CD_3CN, 298 K) δ 8.12 (dd, 2H), 7.89 (dd, 2H), 7.46 (d, 2H), 7.10 (dd, 2H).

Fraction 2. $[Ru(d_8\text{-bipy})_2(pytr\text{-}bipy)Ru(d_8\text{-bipy})_2](PF_6)_3$ (**7d**). Yield after purification: 5.4%. ^1H NMR (CD_3CN, 298 K) δ 8.71–8.65 (m, 2H), 8.54 (m, 1H), 8.31 (d, 1H), 8.07–8.12 (m, 2H), 7.97 (dd, 1H), 7.79 (d, 1H), 7.58 (d, 1H), 7.45 (t, 1H), 7.25 (dd, 1H).

Fraction 3. $[Ru(d_8\text{-bipy})_2(bisbipy)Ru(d_8\text{-bipy})_2](PF_6)_4$ (**3d**). Yield after purification: 5.8%. ^1H NMR (CD_3CN, 298 K) δ 8.62 (dd, 4H), 8.07 (dd, 4H), 7.73 (d, 4H), 7.43 (dd, 2H).

Ni(0) coupling reactions using 1a and 2b as precursors

$[Ru(bipy)_2(pytr\text{-}bipy)Os(bipy)_2](PF_6)_3$ (**8**) $[Os(bipy)_2(bipy\text{-}bipy)Os(bipy)_2](PF_6)_4$ (**4**) and $[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_2$ (**5**) were prepared from $[Ru(Brpytr)(bipy)_2](PF_6)$ (**1a**) (0.71 mmol) and $[Os(Brbipy)(bipy)_2](PF_6)_2$ (**2b**) (0.71 mmol) using the method described above. Crude yield: 0.82 g, (95%).

Fraction 1. This compound was identified (*vide supra*) as $[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_2$ (**5**). Yield after purification: 8.2%.

Fraction 2. $[Ru(bipy)_2(pytr\text{-}bipy)Os(bipy)_2](PF_6)_3\cdot NaNO_3$ (**8**). Yield after purification: 8.5%. ^1H NMR (CD_3CN, 298 K) δ 8.58–8.46 (m, 12H), 7.95–7.75 (m, 12H), 7.71–7.52 (m, 8H), 7.62 (d, 4H), 7.39–7.28 (m, 10H). Elem. anal. $RuOsC_{57}H_{43}N_{14}P_3F_{18}\cdot NaNO_3$: Calc: C 39.44%, H 2.47%, N 12.11%. Found: C 38.38%, H 2.44%, N 12.46%. ESI-MS $[M - 3PF_6]^{3+}$, $m/z = 405.4$.

Fraction 3. $[Os(bipy)_2(bipy\text{-}bipy)Os(bipy)_2](PF_6)_4\cdot KNO_3$ (**4**). Yield after purification: 7.9%. ^1H NMR (CD_3CN, 298 K) δ 8.58–8.46 (m, 12H), 7.95–7.75 (m, 12H), 7.71–7.52 (m, 8H), 7.62 (d, 4H), 7.39–7.28 (m, 10H). Elem. anal. $Os_2C_{60}H_{46}N_{12}P_4F_{24}\cdot KNO_3$: Calc: C 36.29%, H 2.31%, N 9.17%. Found: C 35.85%, H 2.46%, N 8.88%.

Ni(0) coupling reactions using 1b and 2a as precursors

$[Os(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3$ (**9**) $[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4$ (**3**) and $[Os(bipy)_2(pytr\text{-}pytr)Os(bipy)_2](PF_6)_2$ (**6**) were prepared from $[Os(Brpytr)(bipy)_2](PF_6)$ (**1b**) (0.7 mmol) and $[Ru(Brbipy)(bipy)_2](PF_6)_2$ (**2a**) (0.7 mmol) using the method described above. Crude yield: 0.81 g (95%).

Fraction 1. $[Os(bipy)_2(pytr\text{-}pytr)Os(bipy)_2](PF_6)_2\cdot H_2O$ (**6**). Yield after purification: 7.9%. ^1H NMR (CD_3CN, 298 K) δ 8.44–8.36 (m, 8H), 8.06 (dd, 2H), 7.81–7.62 (m 16H), 7.39 (d, 2H), 7.27–7.20 (m, 8H), 7.16 (t, 2H), 7.01 (t, 2H). Elem. anal. $Os_2C_{54}H_{40}N_{16}P_2F_{12}\cdot H_2O$: Calc: C 40.50%, H 2.62%, N 14.00%. Found: C 40.59%, H 2.51%, N 13.57%.

Fraction 2. $[Os(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3\ NaNO_3$ (**9**). Yield after purification: 8.4%. ^1H NMR (CD_3CN, 298 K) δ 8.60–8.43 (m, 11H), 8.14–8.03 (m, 6H), 7.97 (t, 1H), 7.89–7.77 (m, 12H), 7.61 (d, 1H), 7.52 (d, 1H), 7.42–7.24 (m, 10H), 7.08 (dd, 1H). Elem. anal. $RuOsC_{57}H_{43}N_{14}P_3F_{18}\cdot NaNO_3$: Calc: C 39.44%, H 2.47%, N 12.11%. Found: C 38.91%, H 2.43%, N 12.44%.%. ESI-MS $[M - 3PF_6]^{3+}$, $m/z = 405$.

Fraction 3. This material was identified as $[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4$ (**3**). Yield after purification: 7.9%.

Physical measurements

^1H NMR spectra were recorded on a Bruker (AC) (400 MHz) NMR spectrometer. All measurements were carried out in $CDCl_3$ for ligands and in d_3-acetonitrile for complexes. Peak positions are relative to residual solvent peaks. UV/vis absorption spectra were recorded on a JASCO 570 UV/Vis-NIR or a JASCO 630 UV/Vis spectrophotometer with 1 cm pathlength quartz cells. Absorption maxima are ±2 nm: molar absorptivities are ±10%. Emission spectra were recorded at 450 nm at 278 K in spectroscopic grade solvents using a JASCO-7200 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 detector. Emission lifetime measurements were carried out using Time Correlated Single Photon Counting (Edinburgh Analytical Instruments) in a T setting, consisting of a nF900 (N_2 filled) flashlamp, J-yA monochromators, a Single Photon Photomultiplier Detection System, model S 300 detector, with a Norland N5000 MCA card. The F900 Program, (Version 5.13) is used for data processes, with the quality of fits determined by examination of the χ^2 and residual plots of the fitted functions. Lifetimes were recorded in aerated acetonitrile and are ±10 ns. Mass spectra were recorded using a Bruker-EsquireLC_00050 using electrospray ionisation using a cap-exit voltage of 167 V. Spectra were recorded in the scan range of 50–2200 m/z with an acquisition time of between 300 and 900 μs and a potential of between 30 and 70 V. Each spectrum was recorded by the summation of 20 scans. Elemental analysis was carried out at the Microanalytical Laboratory at University College Dublin.

Results and discussion

Synthetic aspects

The synthesis of large supramolecular assemblies is by no means straightforward, especially when the desired product is heteronuclear in nature and is based upon an asymmetric bridging ligand such as the bipyridine-triazole based ligand shown in Fig. 1. When such ligands, which can be prepared without great difficulty, are reacted directly with $M(bipy)_2$-moieties a range of products may be expected. With triazole based systems, in addition, two positional coordination isomers can be expected also, since the metal ions may coordinate at the N2 or the N4 atom of the triazole ring. For example, direct reaction of Hpytr-Hpytr to form dinuclear compounds leads to the formation of up to eight isomers.[9]

An alternative synthetic approach is therefore necessary to avoid the formation of so many different species. The most obvious and direct route to such dinuclear compounds is *via* Suzuki cross-coupling reactions using, for example, organohalide substituted bipy and boronic acid modified pyridyltriazole precursor complexes.[10] However, despite repeated attempts to proceed *via* this route using a range of precursors, catalysts and conditions, the target products were not obtained, possibly because of the electronic properties of the triazole moiety. However, it we demonstrated previously that with Ni(0) as a catalyst a homogenous cross-coupling of triazole containing precursors can be achieved.[3a,b,d] It was, therefore, decided that this route would be pursued. The $M(bipy)_2$-type precursor complexes **1** and **2** (Fig. 2)

were used as bromo-precursors. Importantly, such compounds are readily accessible. The results obtained show that the bromine functional group allows for efficient coupling of the mononuclear complexes using this Ni(0) catalysed reaction. Furthermore, the presence of the bromine substituent at the 3′ position of the triazole ring results in the preferential formation of the N2 isomer (>95%) of complexes **1a**, **1b** and **1d**. This reduces the number of isomers that may be obtained for the mononuclear precursors and hence the dinuclear complexes formed in subsequent reactions. One disadvantage of this method is that, since the Ni(0) catalysed coupling reaction is in essence a homogeneous cross-coupling reaction, three different compounds will be obtained each containing a different bridging ligand as shown in Fig. 3. As outlined in the Experimental section the compounds obtained may be separated using silica and Sephadex based column chromatography based on their respective charges with the dicationic complex as the first fraction, the target tricationic complex as the second fraction, and finally the tetracationic complex.

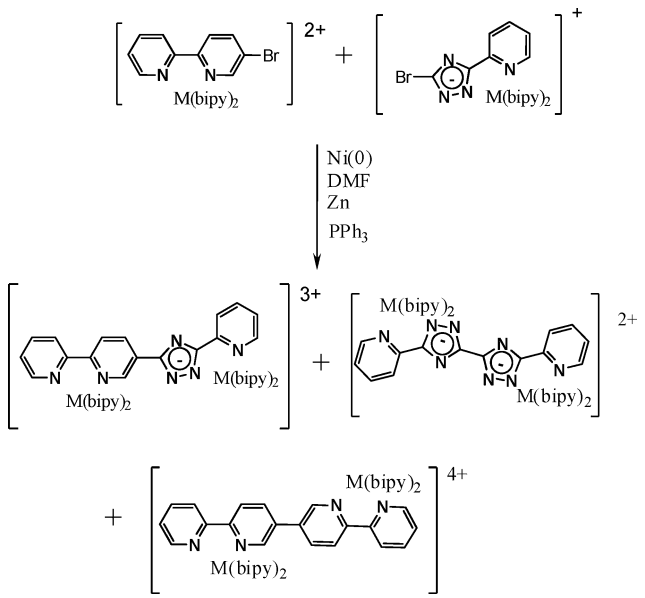

Fig. 3 Synthetic approach used for the synthesis of the dinuclear complexes.

In general yields after purification were moderate, with ruthenium and osmium dinuclear complexes being obtained in approximately 5–8.5% isolated yield with respect to the crude yield under non-optimised conditions. Considering that three different products are formed the expected statistical yield for each product will be about 33% assuming that the reactivity of both reaction components is similar. A similar synthetic approach has been reported by Scandola and co-workers who isolated one of the three possible products.[3f]

The effect of variation of the concentration of the reactants on the reaction product distribution was investigated to assess the reactivity of the two reaction partners **1a** and **2a** as shown in Table 1. The data obtained indicate that by increasing the molar equivalents of precursor complex $[Ru(bipy)_2(Brbipy)](PF_6)_2$ and leaving the molar equivalent of the second precursor complex the same, the percentage yield obtained for the target compound $[Ru(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2](PF_6)_3$ (**7**) and for

Table 1 Effect of ratio of reactants on isolated yields

Precursor	Molar ratio	Yield **7**	Yield **3**	Yield **5**
1a/2a	1 : 1	7.6% (92 mg)	8.0% (96 mg)	8.1% (97 mg)
1a/2a	2 : 1	8.0% (14 mg)	9.7% (17 mg)	2.8% (5.0 mg)
1a/2a	1 : 2	7.6% (14 mg)	2.4% (4.5 mg)	9.1% (16 mg)

$[Ru(bipy)_2(bipy\text{-}bipy)Ru(bipy)_2](PF_6)_4$ (**3**) remain the same, while a decrease in the percentage yield of complex **5**, $[Ru(bipy)_2(pytr\text{-}pytr)Ru(bipy)_2](PF_6)_3$ is observed. When the ratio of reactants is reversed the yield of compound **3** is reduced while that of the others is maintained.

These results indicate that the percentage yield of one of the dinuclear products may be reduced significantly by control of the concentration of the precursor complexes, which simplifies the purification process. These results furthermore indicate that the reactivity of the reactants used is similar.

^{1}H NMR Spectroscopy

The ^{1}H NMR data obtained for all compounds are listed in the Experimental section. The ^{1}H NMR spectra of the asymmetric compound $[Ru(bipy)_2(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$ (**7**), and its d_8-bipy isotopologue **7d** are shown in Fig. 4.

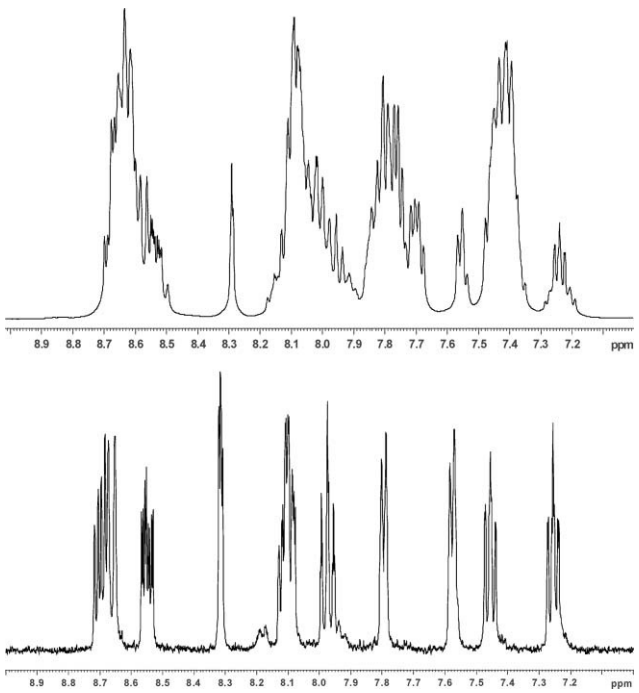

Fig. 4 ^{1}H NMR spectra of **7** (top) and **7d** (bottom) in d_6-acetonitrile.

The interpretation of the resonances observed is made by comparison with related compounds, COSY and deuteriation of the bipy ligands. Overall the results obtained for the bipy ligands are as expected[11] and are not considered further. The spectra obtained for the asymmetric compounds are more complex than those of the symmetric dinuclear complexes. However, as shown in Fig. 4, the spectra can be simplified considerably by preparing the partly deuteriated complexes. Using the spectra obtained for these deuteriated compounds the ^{1}H NMR absorptions of the bridging ligand can be determined accurately (Fig. 5).

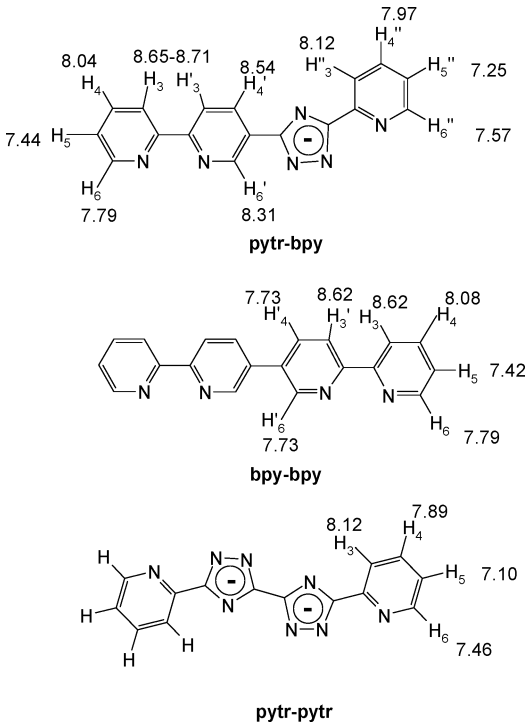

Fig. 5 ^{1}H NMR spectroscopic data for bridging ligands in the dinuclear complexes.

The ^{1}H NMR spectra support the formation of the dinuclear compounds. In addition, the utilisation of deuteriated bipy ligands facilitates the full assignment of the bridging ligand ^{1}H NMR absorption bands.

Electronic properties

Electronic absorption and emission data for all complexes are presented in Table 2. All complexes exhibit absorption and emission properties which are characteristic of Ru(II) and Os(II) based polypyridyl complexes with triazole and/or bipyridyl bridging ligands (Fig. 7).[3] The characteristic dπ–π* metal to ligand charge transfer (^{1}MLCT) absorption bands are observed in the visible region (350–520 nm). For the bis-1,2,4-triazolato containing complex **5** the ^{1}MLCT absorption bands are red-shifted compared with those complexes containing one (**7**) or no (**3**) 1,2,4-triazolato units due to the increased σ-donor capacity of this moiety. Similar spectral features are observed for the corresponding Os(II) complexes (**4**, **6** and **8**). However additional absorption bands are observed in the 500–700 nm region characteristic of ^{3}MLCT absorption bands typical of Os(II) polypyridyl compounds.

Table 2 Electronic properties of dinuclear complexes

	λ_{max}(abs)/nm ($10^{-4}\varepsilon$/M^{-1} cm^{-1})	λ_{max}(em)/nm (τ/ns)
3	440 (2.53)	663 (215)
4	463 (2.57), 625 (0.47)	792 (85)
5	478 (1.90)	686 (62)
6	496 (2.67), 652 (0.61)	811 (15)
7	447 (1.76)	668 (80)
8	445 (1.23). 622 (0.16)	738 (50)
9	456 (1.68), 501 (1.18)	790 (12)
$[Ru(bipy)_3]^{2+}$	450 (1.30)	615 (170)
$[Os(bipy)_3]^{3+}$	468 (1.11)	732 (60)

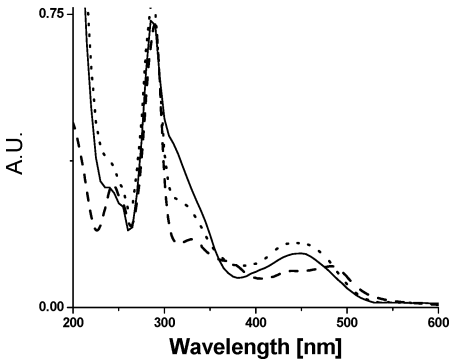

Fig. 6 UV/Vis absorption spectra of $[(bipy)_2Ru(bis\text{-}bipy)Ru(bipy)_2]^{4+}$ (**3**) (solid line), $[(bipy)_2Ru(pytr\text{-}pytr)Ru(bipy)_2]^{2+}$ (**5**) (dashed line) and $[(bipy)_2Ru(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$ (**7**) (dotted line) in acetonitrile. Spectral intensities were adjusted for comparison.

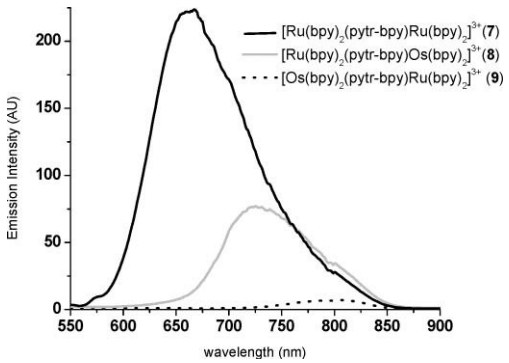

Fig. 7 Emission spectra of compounds **7–9** in CH_3CN. Solutions were isoabsorptive at the wavelength of excitation (450 nm). Counter-anion of complexes **7–9** is PF_6^-.

All complexes exhibit the expected ^{3}MLCT based luminescence at room temperature in acetonitrile solution (Table 2 and Fig. 7).[3,12] As observed for the absorption spectra there is a general shift to lower energy with increasing number of σ-donor triazolato moieties. For the heteronuclear complexes, **8** and **9**, emission is observed only from the osmium centre. This indicates that in the excited state interaction between the two metal centres is significant. At this stage it is however not possible to identify the ligand localisation of the emitting ^{3}MLCT state definitively. For the compounds based either on the Hpytr-Hpytr bridging ligand the emissive ^{3}MLCT state is most probably based on peripheral bipy ligands.[3a,b] However for the bipy-pytr and bipy-bipy bridged complexes the situation is less clear. In these compounds the emitting state may be based on the bridging ligand or on the peripheral bipyridyl ligands. The absorption spectrum shown for $[(bipy)_2Ru(bis\text{-}bipy)Ru(bipy)_2]^{4+}$ in Fig. 6 is of interest in this respect. For this compound a strong shoulder in the UV region is shown at 330 nm. This feature is not present in the other compounds and may be indicate lower energy π–π* transitions in the bridging ligand.

Conclusions

The results reported in this study show that homogeneous coupling technologies can facilitate direct access to asymmetric bimetallic compounds which cannot be obtained in other ways. Because of the homogeneous nature of this approach, three compounds are obtained from a single reaction: the target compound with the asymmetric bridging ligand, and two reference compounds based on the symmetric analogues. In this way a series of related compounds can be made where not only the nature of the bridging ligand, but also that of the two metal centres attached can be changed systematically. It is also important to note that in this manner new bridging ligands can be prepared *in situ.* To the best of our knowledge the bpy-bpy, or 2,2′:5′,5″:2″,2‴-quaterpyridine, and Hpytr-bpy ligands have not been prepared before, while for the Hpytr-Hpytr bridging ligand pure compounds can only be obtained by this synthetic approach. A number of related quaterpyridine ligands such as 2,2′:6′,2″:6″,2‴- 2,2′:4′,4″:2″, 2‴-, 2,2′:3′,2″:6″,2‴-, 4,4′:2′,2″:4″,4‴-quaterpyridine and 2,2′:4′,2″:6″,2‴-quaterpyridine have appeared in the literature.[13] Our interest in these compounds is aimed at the investigation of the electronic properties and interaction between metal centres in dinuclear assemblies, both in the ground and excited state. With the compounds presented here, a systematic investigation of these supramolecular aspects as a function of the HOMO and LUMO properties of the bridge and those of the metal centres will be carried out. Importantly the distance between the metal centres in the compounds remains the same but the electronic properties of the bridge are very different. Further investigation of the intramolecular interaction of these dinuclear compounds in the excited state using emission and resonance Raman spectroscopy and in the ground state by applying electrochemical and spectro-electrochemical techniques, will be reported in due course.

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